



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

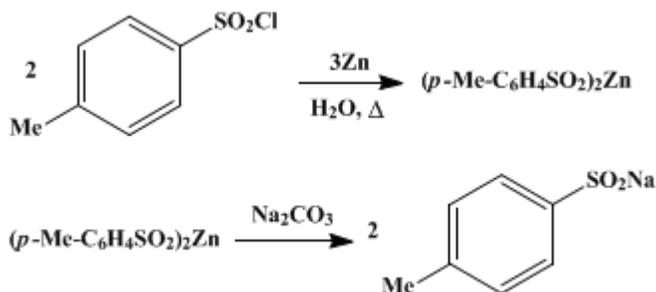
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.492 (1941); Vol. 2, p.89 (1922).*

## SODIUM *p*-TOLUENESULFINATE

[*p*-Toluenesulfinic acid, sodium salt]



Submitted by Frank C. Whitmore and Frances H. Hamilton.

Checked by J. B. Conant and Paul Allen, Jr.

### 1. Procedure

Five hundred grams (2.6 moles) of technical *p*-toluenesulfonyl chloride is ground in a mortar to break up all lumps. Three liters of water is placed in a 12-l. crock provided with a large brass stirrer and a tube for passing steam directly into the liquid. Dry steam is passed into the water until the temperature reaches 70°. The steam is then shut off and 400 g. (5.5–6.1 atoms) of zinc dust (90 to 100 per cent pure) is added. The sulfonyl chloride is then added in small portions by means of a porcelain spoon. The addition takes about ten minutes. The temperature rises to about 80°. Stirring is continued for ten minutes after the last of the chloride has been added. Steam is then passed into the mixture until the temperature reaches 90°. If it is heated any hotter, bumping takes place. The steam is shut off, and 250 cc. of 12 *N* sodium hydroxide solution is added. Finely powdered sodium carbonate is then added in 50-g. portions until the mixture is strongly alkaline. The mixture froths considerably, but this causes no trouble unless too small a crock is used. The stirrer is loosened and the crock is removed.

The mixture is filtered by suction in a large funnel. The filtrate has a volume of about 4.5 l. The cake of unchanged zinc dust and zinc compounds is transferred to a 3-l. battery jar and placed under the stirrer, and the latter is clamped in place. Water (750 cc.) is added, the stirrer is started, and steam is passed in until the mixture starts to froth too violently. The steam is then shut off, but the stirring is continued for ten minutes. The mixture is filtered and the filtrate is added to the main solution in a large evaporating dish. The liquid is evaporated over a large burner to a volume of about 1 l., or until a considerable crust forms around the edges. The mixture is then cooled. Large, flat, transparent crystals separate. The thoroughly cooled mixture is filtered by suction, and the crystals are air-dried until efflorescence just starts. They are then bottled. The product is *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Na·2H<sub>2</sub>O. The yield is 360 g. (64 per cent of the theoretical amount). Careful acidification of the mother liquor with dilute hydrochloric acid yields 15 g. of the free sulfinic acid (Note 1).

### 2. Notes

1. The free sulfinic acid may be prepared by dissolving the sodium salt in cold water and carefully acidifying the solution with hydrochloric acid. An excess of hydrochloric acid must be avoided, as it dissolves the acid to a certain extent. The sulfinic acid is difficult to dry without partial conversion into the sulfonic acid and thiosulfonic ester.

It is suggested that an office ledger press is convenient for rapid drying between sheets of filter paper (D. T. Gibson, private communication).

### 3. Discussion

*p*-Toluenesulfinic acid and its salts can be prepared by the following general methods: the reduction

of the sulfonyl chloride by sodium amalgam,<sup>1</sup> zinc dust in alcohol and water,<sup>2</sup> sodium sulfite,<sup>3</sup> sodium sulfide,<sup>4</sup> potassium hydrosulfide<sup>5</sup> (the thio acid being first formed), and sodium arsenite;<sup>6</sup> from toluene, aluminum chloride, sulfur dioxide, and hydrogen chloride;<sup>7</sup> from *p*-toluidine by diazotization and subsequent treatment with sulfur dioxide and finely divided copper;<sup>8</sup> and from *p*-tolylmagnesium bromide and sulfur dioxide.<sup>9</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 519
- Org. Syn. Coll. Vol. 4, 937

---

## References and Notes

1. Otto, Ann. **142**, 93 (1867).
2. Schiller and Otto, Ber. **9**, 1586 (1876).
3. Blomstrand, Ber. **3**, 965 (1870).
4. Meister, Lucius, and Brüning, Ger. pat. 224,019 [Chem. Zentr. II, 513 (1910)].
5. Fromm and Erfurt, Ber. **42**, 3821 (1909).
6. Gutmann, Ber. **41**, 3351 (1908); Ber. **42**, 480 (1909).
7. Knoevenagel and Kenner, Ber. **41**, 3318 (1908); Smiles and LeRossignol, J. Chem. Soc. **93**, 754 (1908).
8. Gattermann, Ber. **32**, 1141 (1899); Thomas, J. Chem. Soc. **95**, 344 (1909).
9. Unpublished directions.

---

## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfinic acid

sulfonic acid

thiosulfonic ester

$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Na}\cdot 2\text{H}_2\text{O}$

*p*-Toluenesulfinic acid and its salts

alcohol (64-17-5)

hydrogen chloride,  
hydrochloric acid (7647-01-0)

sodium sulfite (7757-83-7)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

sulfur dioxide (7446-09-5)

copper (7440-50-8)

sodium arsenite

aluminum chloride (3495-54-3)

toluene (108-88-3)

zinc (7440-66-6)

sodium (13966-32-0)

sodium sulfide (1313-82-2)

potassium hydrosulfide (1310-61-8)

p-toluidine (106-49-0)

p-Toluenesulfonyl chloride (98-59-9)

p-tolylmagnesium bromide (4294-57-9)

p-toluenesulfinic acid, sodium salt,  
Sodium p-toluenesulfinate